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DETERMINATION OF CARBON IN STEELS AND IRONS BY DIRECT COMBUSTION IN OXYGEN AT HIGH TEMPERATURES[1]

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The influence of temperature on the results obtained by the direct combustion of steel and iron in oxygen has been frequently investigated[2] and the general consensus of opinion seems to be that higher results for carbon are obtained with higher combustion temperatures. This conclusion, however, is rendered doubtful by a number of circumstances: (1) Quite frequently, because of uncertainties in blanks it is impossible to conclude whether the difference in results claimed is due to variation in blank or is real; (2) the published work does not indicate that investigators have always assured themselves that the material used to support the drillings or that the fluxes sometimes used are completely free from carbon; (3) differences in carbon results with the same steel are frequently due to a variation in the size of drillings used.

Combustions of steel are ordinarily made in such a way that the oxides are in the fused condition for only a very short time. This is evident from work done here, which shows that the fusion point of the oxides themselves is above 1450°,[3] and that as soon as the fused material has combined with or permeated the bed material the melting point of the combination becomes much higher. The temperature of a combustion furnace as ordinarily operated does not exceed 1200° and usually lies between 950° and 1100°, hence it is evident that the oxides from 1 or 2 grams of steel must solidify very rapidly after the combustion period is over, for it is only during this time that the temperature is above the melting point of the oxides. Burning in the ordinary way, if the sample consists of very large particles there is always the danger of incomplete combustion of all its parts; on the other hand, if the particles are very small the combustion may proceed so rapidly as to cause initial fusion of a portion of the oxides followed by quick solidification of the fused part with resultant inclosure of yet unburned metal. There is some chance, too, that carbon dioxide or monoxide may be inclosed in the solidified mass, and that with certain alloy steels difficult oxidizable carbides (silicon, tungsten, chromium) may escape oxidation except at very high temperatures.

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[1] This paper is an amplification of a preliminary paper on this subject by the same authors. See J. Wash. Acad. Sci., 4, p. 393; 1914.

[2] See Lorenz, Z. Angw. Chem., 6, pp. 313, 395, 411, 635; and Foerster, Z. Anorg. Chem., 8, p. 274, 1895, for work at high temperatures; for references to work at other temperatures, see article by Mueller and Diethelm, Z. Angw. Chem., 27, p. 2114; 1910.

A consideration of these facts, together with previous experimental work here and elsewhere, which showed that oxides from apparently well-burned samples yielded additional carbon upon being finely pulverized and reburned, led to the development of the present method, in which the sources of error cited in the first paragraph are eliminated. The object of this work was to develop a procedure which would give the best possible chance for oxidation and liberation of all the carbon in the sample, regardless of the original size of drillings, and especially to ascertain by such method the order of the error, if any, which affected the carbon determinations reported on the certificates for the Bureau's series of standard analyzed irons and steels. The latter determinations were made as usual either by direct combustion of the metal at temperatures of 950° to 1200°, or else by burning the carbon residue left after solution of the steel or iron in a suitable solvent.[4] Briefly, our method consisted in burning the metal directly in oxygen within the usual temperature range, then raising the temperature to a point above the fusion point of the oxides and maintaining this temperature long enough to insure that all parts of the sample had been brought in contact with oxygen or fused iron oxide. The sample was burned directly on platinum (with precautions described later), so that no carbon could be obtained from the support for the drillings; the carbon was estimated by the barium carbonate titration method devised by one of the authors[5] and in such way that the blank was negligible.

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[3] By G. K. Burgess and R. G. Waltenburg, unpublished.

[4] In a few cases certificate results include the carbon obtained from reburning the oxides.

It seemed first desirable to know whether carbon dioxide or monoxide were left inclosed in the oxides produced during the direct combustion process as ordinarily carried out. To determine this there was used an apparatus consisting of an evolution flask connected to a suitable purifying train followed by absorption tubes for carbon dioxide and monoxide.[6] In the evolution flask there was placed a large excess of concentrated hydrochloric acid together with the uncrushed oxides resulting from the combustion in the ordinary way (on pure alundum) of twenty-two 2-gram samples of steels known to yield carbon upon reburning after pulverizing. Boiling the contents of the flask for several hours resulted in complete solution of everything except the mechanically held alundum, and during this time a current of air purified from carbon dioxide and monoxide was passed through the apparatus. The carbon dioxide found in the absorption tube was 0.00104 gram, which would correspond to 0.0007 per cent carbon on the basis of 44 grams of metal taken; the absorption tube for carbon monoxide showed none of this gas to be present. It seems fair to conclude from this experiment that any error in ordinary combustions resulting from occlusion or inclusion of carbon dioxide or monoxide is quite negligible. The case might be different where silica is used as supporting material for drillings, and there is consequently the possibility of forming viscous, slowly solidifying slags which might well retain large bubbles of gas. It should be noted in this connection that immediately after the combustion of metal has ceased the partial pressure of carbon dioxide and monoxide inside the combustion tube reaches a maximum because the incoming oxygen has been almost completely consumed by the metal, leaving but little excess to sweep on the products of combustion; the oxides begin to freeze very soon after, and accordingly conditions are then very favorable for retention of carbon dioxide or monoxide by the solidifying oxides. However, as stated, when nonviscous, quickly solidifying oxides result, as in our experiment, the error from this cause may be regarded as negligible.

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[5] J. R. Cain, B. S. Tech. Paper No. 33; J. Ind. and Eng. Chem., 6, p. 465; 1914.

[6] Both palladium chloride and iodine pentoxide tubes were used.

For carrying out combustions under the conditions selected by us—initial temperatures of 1050° to 1100° followed by temperatures above 1450° and burning the metal directly supported on platinum—it was necessary either to start with low temperatures and slow oxygen current, increasing both as the skin of oxide on the grains became thick enough to protect the platinum, or else to burn initially in a furnace kept at the lower temperatures and then transfer the boat and contents to the high-temperature furnace. The first method was carried out in the gas furnace shown in Figs. 1 and 2;[7] the second procedure was used with our usual nichrome-wound furnaces in conjunction with the platinum-wound furnace shown in Fig. 3. In view of the failure to find notably higher results by our method (as will appear later), we did

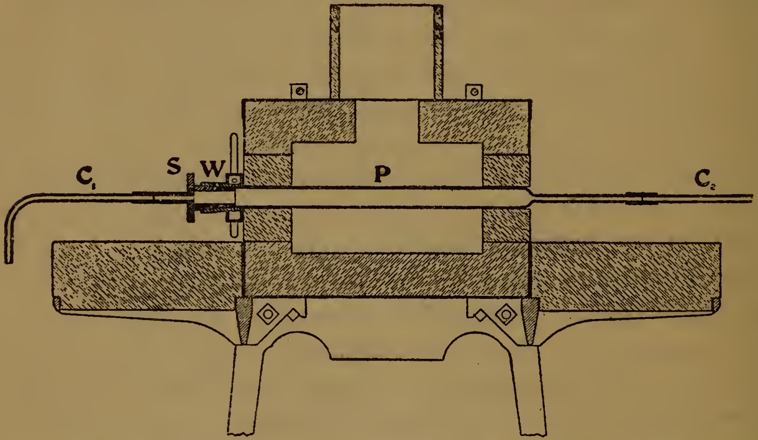

FIG. 1.—*Cross section of gas furnace.* C_1, C_2, *copper tubes soldered to platinum tube;* S, *German silver stopper;* W, *water jacket*

not deem it worth while to proceed to the next obvious step in apparatus—the construction of a single electric furnace suitable for both stages of the combustion. The electric-furnace method is very much to be preferred. The required temperatures are reached and maintained with much greater regularity and convenience than when gas is used, the wear on the platinum is less, and the chance for error from extraneous carbon dioxide is eliminated. The gas furnace is very destructive in its effects on the combustion tube, but the boats seem to suffer very little by either method. If, however, the operation of the gas furnace is conducted carelessly, so that the temperature initially is caused to rise too rapidly and the fusion temperature of the oxides is reached before all the iron is burned, then a boat is soon destroyed by alloying with iron; this is also the case if the combustion of metal is incomplete in the first electric furnace when using that method. Temperatures were measured with a Wanner optical pyrometer and with a platinum-iridium thermo-element in conjunction with a millivoltmeter. The low-temperature electric furnace was maintained at 1050° to 1100°, the high-temperature electric furnace at 1475°; the gas furnace was started from room temperature and raised gradually to 1525°, at which temperature it was held during the fusion period. The copper oxide catalyzer following the furnace was found absolutely necessary when using the gas furnace, otherwise very large amounts of carbon monoxide were produced and escaped absorption; the low-temperature electric furnace also contained heated copper oxide in the forward portion of the (porcelain) combustion tube.

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[7] Reproduced from our first paper on high-temperature carbon combustions, above cited.

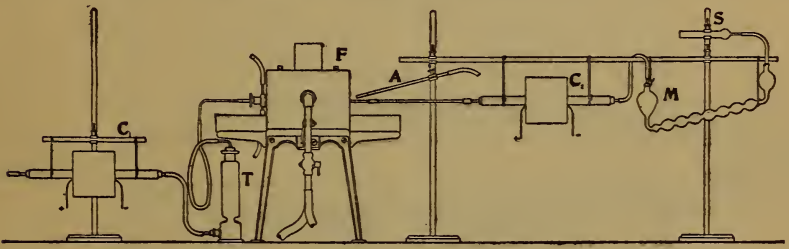

FIG. 2.—*Apparatus for high temperature combustions.* A, *air cooling tube;* C_1, C_2, *copper oxide catalyzers;* F, *gas furnace shown in Fig. 1;* M, *Meyer tube;* S, *soda lime tube;* T, *caustic potash jar*

The routine followed in making a determination in the gas furnace consisted in inserting into the combustion tube the boat holding the sample and connecting up the Meyer tube containing barium hydroxide solution. While passing a slow current of oxygen the combustion tube was brought to 700° or 800° and kept within these temperatures for a minute or two until the superficial oxidation of the particles was effected; then the temperature was raised to 1050° or 1100° and the combustion of the iron completed. As soon as absorption of oxygen by the burning metal had ceased the blowpipe flame was turned on full, this stage of the combustion being continued 25 to 30 minutes. The Meyer tube was disconnected and the determination finished by filtering off and washing the precipitated barium carbonate and titrating it against standard acid as described in the cited paper on this method. The procedure when using the electric-furnace method was to place the boat containing the sample in the already heated nichrome furnace, starting with a very slow current of oxygen, increasing gradually to the rate usually maintained and holding this condition until all the metal was burned and the carbon

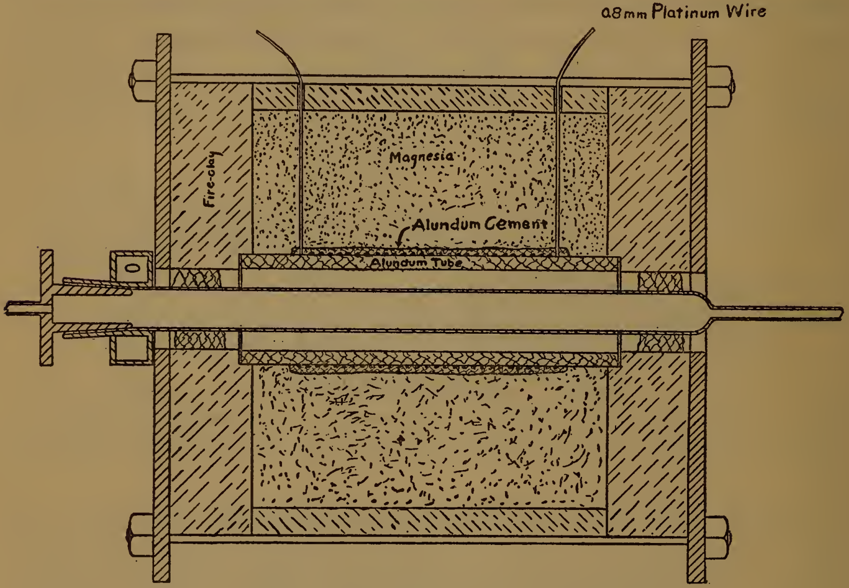

FIG. 3.—*Electric furnace for high temperature combustions*

dioxide swept out of the combustion tube. Then the connection of the Meyer tube was changed to the near-by high-temperature furnace through which oxygen was passing and the boat was transferred quickly to this furnace, which was maintained continuously at the proper temperature. After remaining in the high-temperature furnace 15 to 20 minutes the Meyer tube was disconnected and the filtration and titration finished as before. The oxides were usually found to be thoroughly fused and to have spread over the bottom of the boat; in some cases they even crept over the sides of the container. A second fusion of such oxides gave no further carbon dioxide to a freshly filled and clear barium hydroxide tube.

Great care was taken at all stages of the work to eliminate extraneous carbon dioxide or other substances that would cause a blank, so that, as already stated, the blank was always negligible. The frequent blanks which were made during this work were carried out (1) without any steel in the furnace; (2) when burning Bureau of Standards standard steel No. 23, which, as shown in the table of results in this paper, gives identical values when burned in the ordinary way and by our modified method. The fused oxides were readily removed from the boats, in preparation for the next combustion, by digesting in strong hydrochloric acid for a few hours.

The results in the table show that some steels give higher results by the new method than are shown on the certificates, others yield only slightly higher figures, and still others give the same results by both methods. We find it impossible to relate these three classes with the size of drillings used, with the carbon content of the sample, or especially with the presence or absence of the usual alloying elements. In only two cases were the results by the modified method as much as 0.02 per cent higher than the certificate value; with most of the other samples the difference was of the order of 0.01 per cent. Our work does not cover the Bureau's complete series of standard analyzed steels and irons, but the results are deemed quite representative, and we believe they are complete enough to justify us in the conclusion that the certificate values for these steels can not be affected with an error greater than 0.015 per cent (probably minus), and in most cases the error is much less. It is believed that such errors are negligible, considering the uses to which these standards are at present being put.

Results on Bureau of Standards Standard Irons and Steels

Description and Bureau of Standards number of sample	Certificate value for carbon—Average of all methods	Results obtained by combustion at high temperatures		Difference (average values—certificate values)
		Individual results	Average values	
Bessemer:				
0.1 per cent C, No. 8a	0.084	0.086	0.087	+0.003
		.088		
		.088		
		.086		
		.086		
0.4 per cent C, No. 10b	[a].373	.371	.372	− .001
		.370		
		.374		
		.374		
0.8 per cent C, No. 23	.805	.800	.805	.000
		.806		
		.805		
		.805		
		.804		
		.809		
		.805		
		.804		
B. O. H.:				
0.1 per cent C, No. 15a	.111	.116	.117	+ .006
		.116		
		.118		
		.116		
		.118		
0.4 per cent C, No. 12a	.364	.379	378	+ .014
		.379		
		.376		
		.376		
		.379		
0.8 per cent C, No. 14a	.815	.819	.816	+ .001
		.816		
		.816		
		.816		
		.812		
A. O. H.:				
0.2 per cent C, No. 19a	207	.214	216	+ .009
		.218		
		.218		
		.214		
0.6 per cent C, No. 21	.591	.602	.600	+ .009
		.598		
		.602		
		.598		

[a] Certificate value, direct combustion, 0.363.

Results on Bureau of Standards Standard Irons and Steels—Continued

Description and Bureau of Standards number of sample	Certificate value for carbon—Average of all methods	Results obtained by combustion at high temperature		Difference (average values—certificate values)
		Individual results	Average values	
A. O. H.—Continued				
1 per cent C, No. 35	1. 03	1. 052	1. 05	+0. 02
		1. 048		
		1. 045		
		1. 052		
		1. 048		
Alloy steels:				
Chrome vanadium, No. 30	.373	.382	.379	+ .006
		.375		
		.379		
		.379		
		.381		
		.381		
		.379		
Chrome nickel, No. 32	.372	.383	.383	+ .011
		.380		
		.386		
		.383		
		.380		
		.383		
Chrome tungsten, No. 31	.599	.610	.609	+ .010
		.610		
		.608		
		.608		
		.612		
		.609		
		.609		
Nickel steel, No. 33	.278	.282	.285	+ .007
		.280		
		.289		
		.285		
		.288		
Vanadium steel, No. 24	.348	.350	.352	+ .004
		.350		
		.354		
		.353		
Irons:				
Iron C, No. 5b	2. 726	2. 74	2. 743	+ .017
		2. 75		
		2. 74		
Iron D, No. 6a	2. 46	2. 48	2. 48	+ .02
		2. 48		
		2. 48		

The experimental difficulties and the inconvenience of this method of determining carbon place it beyond the reach of most industrial and works laboratories, and we do not, therefore, recommend its use to such, except in the case of products for which it may be found better adapted than other methods.

WASHINGTON, November 3, 1915.

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